

Methods for Determination of Moisture

Oven Drying

C. O. WILLITS

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

THE determination of moisture in organic materials, whether they be synthetics or biological materials, is not a simple procedure. Even today a common concept of moisture analysis that implied by an old (1885) procedure of the Association of Official Agricultural Chemists, which specified moisture as the loss in weight occurring when a substance was heated at 98° to 100° C. This simple method will give approximate moisture values, but cannot be depended upon to produce accurate results because it fails to recognize the complexity of the process of water removal. The results obtained by the time-honored thermal drying methods may sometimes be wrong, but nevertheless oven methods for moisture analysis generally are the standard for most other moisture methods, whether by distillation, electric moisture testers, chemical reactions, or some other physical means.

During the heating of a moist organic substance the following

changes may be expected to occur: volatilization of water as moisture, volatilization of other adsorbed material, and volatilization of the gaseous products formed by nonreversible decomposition reactions, such as carbon dioxide, carbon monoxide, methane, hydrogen, and water. This decomposition does not begin at any particular temperature, but goes on at all temperatures at widely different rates.

Nelson and Hulett (5) in 1920 found that when an organic substance was heated at constant temperature the amount of water liberated from that existing as the external phase was dependent upon the temperature and that the rate of removal of this water, liberated by heat at constant temperature, is rapid at first, then falls off, and, in time, ceases. They plotted the per cent moisture against time and obtained isotherms (Figure 1) for successively higher temperatures. When a curve is parallel to the time axis,

it means that no more water is being liberated at that temperature. These curves indicate that the water of the external phase remaining after each heating temperature has such a low vapor pressure that no further loss of water occurs. This low vapor pressure, according to Nelson and Hulett, may be due to successively thinner layers of water, or to other physical phenomena such as capillary attraction and diffusion.

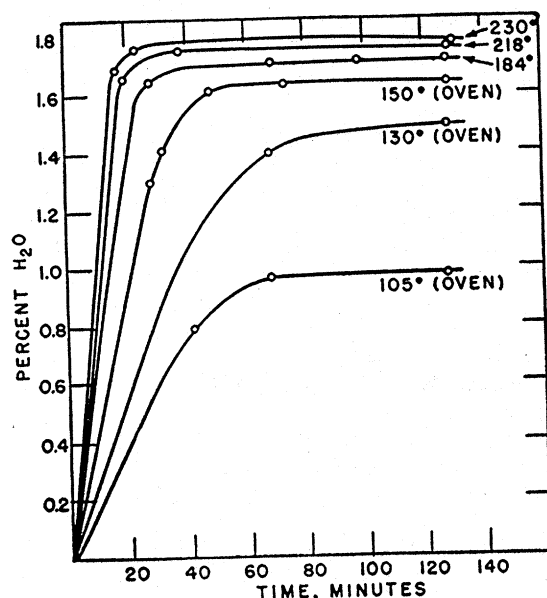


Figure 1. Removal of Water at Constant Temperature

What then is the true moisture, if the one obtained by the 100° C. drying is not an end value, and which curve shows the beginning of losses due to decomposition of the sample? Porter and Willits (7) obtained a similar family of drying isotherms for starch and suggested a means of estimating the temperature at which losses in weight caused by decomposition predominate. If the amount of water liberated, or the loss in weight, is plotted against temperature, the curve shows a distinct break (Figure 2). The first curve indicates loss of external phase water; the second, losses due to volatilization of decomposition products plus water.

A more nearly reproducible method would specify a temperature that would lie on the flattest portion of a moisture-temperature curve. It is unfortunate that organic substances cannot be heated to such a high temperature that all the water molecules

Determination of moisture by oven drying is of great interest, and has been the subject of extensive research and many papers. This resume correlates these studies and the theories and methods of thermal drying, particularly for organic and biological materials. The important factor in thermal drying is the differential between the vapor pressure of the substance to be dried and the vapor pressure of the atmosphere of the drying chamber. A favorable differential can best be attained by use of chemical drying agents rather than by vacuum. The temperature employed should be as high as possible, without causing appreciable thermal decomposition. Guides are given for establishing thermal drying conditions of most organic and biological materials.

must be evolved as a gas. It has been suggested that the lower member of the loss in weight-temperature curve be extrapolated to the critical temperature of water and that the height of this point (5) on the loss-in-weight axis would be the value of the true moisture content of the sample. Unfortunately this cannot be done, as the curve is not a straight line, and because of its changing function it is nearly impossible to establish a mathematical expression for the curve. Therefore, although an absolute moisture value cannot be expected by oven drying methods, it is possible to obtain a value that is relatively close to this and is reproducible, by using a temperature indicated by the flattest portion of the curve and a time sufficiently long to ensure reaching constant weight.

Many investigators have contended that naturally occurring organic substances such as cereals and other plant tissue could not be dried without decomposition of the original moisture-free substance. The foregoing method does not conclusively prove that the dried substance is the unaltered original substance minus its external phase, water.

Several attempts have been made to show that drying can occur without decomposition of the substance.

In the case of starch, Porter and Willits observed a light brown discoloration, indicating an alteration in some of the samples during the time necessary to establish the constancy of weight at 180° C. However, they noted no change in the reflectance or in the solubility of the starch until the constant-weight period was reached. While changes in color and solubility were then indicated, they did not affect the constancy of weight until after nearly 4 hours, when a drastic breakdown or alteration occurred, accompanied by a further loss in weight. Sair and Fetzer (9) measured thermal decomposition by determining "reversibility moisture." It has been known for a long time that completely dehydrated biological products exhibit a hysteresis effect on re-sorption to the original moisture level. Urquhart and Eckersall (10) and Pidgeon and Maass (8) have shown that cellulose which contains 1% of moisture loses it reversibly. Mellon and co-workers (4) have shown similar results for proteins with water contents exceeding 15%. In many biological materials it is relatively easy to remove moisture down to the 1% level, but to remove the final water is difficult. A large number of methods have been proposed to accomplish this. The one most often used is vacuum oven drying, but it is not known what occurs during heating, even though it may be in vacuo. Is externally held water the only volatile given off?

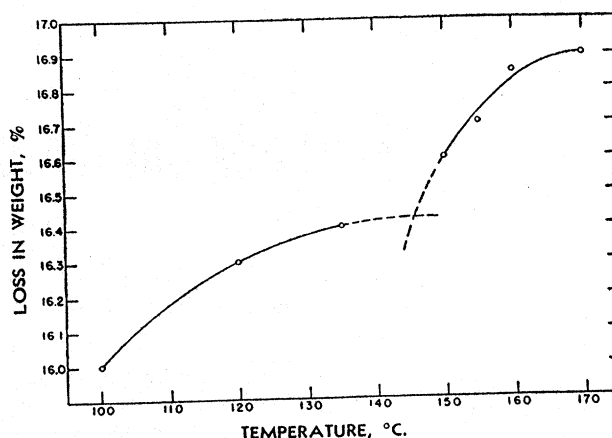


Figure 2. Loss in Weight of Potato Starch Dried at Various Temperatures (7)

Sair and Fetzer (9) applied the technique of reversible drying to cereals to determine whether or not decomposition occurs, or if the original water present in a sample can be accounted for. Using ground corn, a sample was dried at 40° C. for 340 hours, a period well beyond that necessary to attain constant weight. As the weight remained constant, it was considered that the corn was anhydrous. Another sample of the same ground corn was heated at 100° for different lengths of time.

As they assumed that drying at 40° C. for 340 hours resulted in an unaltered, perfectly anhydrous material, why go further?

The answer is simple. A drying period of almost 2 weeks would be impractical in routine analysis and a shorter method utilizing higher temperatures must be used. Their 2-hour drying period, at 100° C. in a vacuum oven, indicated no irreversible changes. However, after 4 hours of heating, the sample on resorption did not have the same dry weight as the control. They considered that two processes occurred, a change in adsorption capacity, and decomposition.

Makower and others (3) also attempted to establish empirical conditions of time vs. temperature, whereby the true moisture could be measured. In work with dehydrated vegetables they became interested in the problem because of the discordant moisture results obtainable on similar samples. The basis of their technique assumes that samples of onions and cabbage dried in vacuo at 60° C. for at least 60 hours become essentially dry. By their procedure such a sample was dried at 60° C. for 100 hours and weighed at intervals to obtain a moisture curve. A known weight of water was then added, and after equilibration was complete, the wetted sample was redried at 60° and weight losses were measured at frequent intervals. The time at which the loss in weight equaled the amount of added water was noted as indicating the time required for drying the original moist sample. This is true only if the two curves are similar.

Makower also had to make three assumptions. The first was that essentially all of the water was removed at the end of the first drying run. This was assumed to be correct moisture, because the long drying period yielded weight loss of only 0.005% per hour and redrying time remained unchanged even when the first drying run was conducted for 40 to 50 hours longer. The second assumption was that weight changes (loss) increased with heating time in the same manner for both drying runs. The third assumption was that a negligible amount of decomposition occurred in drying the sample from higher to lower initial moisture levels. This was taken to be valid because the time of drying was relatively short and temperatures were below those at which appreciable decomposition occurs. The moisture content of the original sample was thus equal to the algebraic sum of the known moisture content of the remoistened sample and the shift along the weight-loss axis found in testing for similarity of the two curves.

THEORY

Moisture may occur in a sample in several ways. The ones of interest here are moisture occurring principally as an external phase, and moisture occurring as one or more molecular layers plus liquid water. The rapidity with which moisture can be distilled from the surface of a solid phase is a function of the water vapor pressures and of the drying temperature.

Recent practice has been to remove moisture from a solid at the lowest possible temperatures. All that is really required is that the partial vapor pressure of water in the gas phase (air) be lower than the vapor pressure of the water in the sample. Thus we can have thermal drying at temperatures below the freezing point of water, as in the case of lyophilization, or at higher temperatures as long as the applied energy (heat) is insufficient to cause noticeable decomposition of the solid undergoing drying. However, at higher temperatures an advantage is gained because the vapor pressure rises rapidly with increase in temperature. Thus, potato starch containing 16% moisture has a water vapor pressure of only 12 mm. at 25° C., but this is raised to 539 mm. at 92° C. Some observers have noted that the temperature effect is even greater when only very small amounts of water are present. Thus, Makower observed that in drying potatoes at 70° C. a difference of only 1° C. produced a change of 0.1% in the moisture.

Katz (2) presented the relationship between the water vapor pressure in the air and the water content of macromolecular substances such as cellulose, casein, starch, and gelatin. A similar relationship was shown by Mellon *et al.* in the water sorption of proteins. The shape of the absorption curve indicates that relatively large amounts of water can be held by these substances at very low water vapor pressures. This would mean that, depending upon the nature of the slope of the curve at high temperatures, changes in the water vapor pressure of the air (or changes in relative humidity) have a great or a small effect upon the water content of the solid being dried.

The vapor pressure of liquid water is not very sensitive to changes in the pressure of the atmosphere. At ordinary tem-

peratures an increase of 1 atmosphere pressure increases the vapor pressure of water by only 0.1%; the fractional increase is less the higher the temperature. It is to be assumed, therefore, that the influence of 1 atmosphere of excess pressure on the vapor pressure of adsorbed water on a solid surface would likewise be negligibly small. The ultimate moisture content to which a solid is reduced by thermal drying should be the same for the same partial pressure of water vapor, regardless of the atmospheric pressure.

The partial pressure of water vapor in air does not vary with temperature. Drying rates depend on the difference between the vapor pressure of the external phase of a solid being dried and the vapor pressure in the air. The increase in the rate of drying due to rise of temperature is not due to the lowering of the vapor pressure in the air, but rather to the increase in the vapor pressure of the water on the solid. The rate of drying can be further accelerated by increasing this water vapor pressure differential through lowering the vapor pressure in the air. This can be accomplished by use of a desiccant or a vacuum.

Assuming that the absolute pressure of water in the air surrounding the sample is the important factor, the benefits of a vacuum are real only when the amount of moisture remaining on the sample becomes so small that its vapor pressure will not influence the vapor pressure of the vacuum chamber air. In practice seldom are vacuum ovens used in moisture analyses operating below 1 mm. of mercury pressure. A much simpler procedure to obtain a low vapor pressure is to diminish the water vapor pressure in the air of an oven by utilizing a chemical drying agent. Table I shows that a number of such drying chemicals (1) can reduce the water vapor pressure far below that which is easily attainable with the usual vacuum oven.

In using a drying agent in the determination of moisture, it has been customary to enclose the sample and the desiccant in the same container, so that the moisture in the atmosphere will not be introduced to the system. Having the desiccant near the sample reduces diffusion time, with gained efficiency. With these facts accepted, it was easy to proceed a step farther and combine the good effects gained from the use of both a vacuum oven and a desiccant. This has been applied extensively in Abderhalden and pistol-type dryers, but seldom in larger vacuum ovens.

If no air were let into the vacuum oven, the pressure of the water vapor in the oven would rise to a value that would make the usefulness of the vacuum oven questionable, especially for samples of high moisture content. There will come a time when the efficiency of the oven will be limited by the rate of water diffusion into the pump. To compensate for a low diffusion rate, a small amount of air is let into the oven to produce a continuous sweeping of the oven chamber. This will not lower the water vapor pressure in the oven. A low vapor pressure in the oven can be obtained if the air is desiccated before it is let into the oven, a scheme most often used in large vacuum ovens. Actually, with the use of predesiccated air an air oven would be as effective as a vacuum oven.

SOURCES OF ERROR IN THERMAL DRYING

Some of the sources of error in thermal drying were reviewed by Reith *et al.* (8).

Nonwater Components. In thermal drying, errors will be introduced if the material being dried contains any substances in addition to water which have an appreciable vapor pressure under the conditions of the drying. These will cause an additional loss in weight of the sample aside from the loss due to water, and because the two are not readily distinguishable, they will cause high "moisture" values.

Chemically Bonded Water. Small quantities of water may be lost through chemical reaction induced by heat as in the case of dextrin formation, inversion of disaccharides, or hydrolysis of proteins.

Nonwater Solvents. Often in the case of preparative organic substances which have been crystallized from such solvents as

alcohol or acetone, moisture (loss in weight) values are too low as indicated by elemental analyses. The incomplete "drying" is caused by these solvents being held by the substances throughout the thermal treatment.

Autoxidation. Chemical changes cause an apparent low moisture due to increased weight of sample by autoxidation, especially in fats and oils.

Decomposition. When the temperature of drying is sufficient to cause thermal decomposition of the substance and the products of this decomposition are volatile, high moisture will result. Errors of this sort are most common with organic substances, but inorganic carbonates, for example, can also decompose.

Most of these errors can readily be avoided, with the possible exception of those caused by nonwater volatile constituents. Three methods that tend to minimize errors due to nonwater volatile constituents are: collection of the volatilized water as ice, use of an absorbent specific to water, and the indirect methods of Makower and Porter.

Table 1. Relative Efficiencies of Drying Agents

(Values of residual H₂O per liter of gas dried at 25° C.)

Drying Agent	H ₂ O, Mg.	Drying Agent	H ₂ O, Mg.
Filter at -104° C.	1.6×10^{-22}	CaBr ₂	0.2
P ₂ O ₅	2×10^{-1}	CaO	0.2
Mg(ClO ₄) ₂	5×10^{-4}	CaCl ₂ (granular)	0.14 to 0.25
Mg(ClO ₄) ₂ · 3H ₂ O	2×10^{-3}	H ₂ SO ₄ , 95.1%	0.3
KOH (fused)	0.002	CaCl ₂ (fused)	0.36
Al ₂ O ₃	0.003	ZnCl ₂	0.8
H ₂ SO ₄	0.003	ZnBr ₂	1.1
MgO	0.008	CuSO ₄	1.4
NaOH (fused)	0.16		

Losses of water through chemical reaction in dextrinization or protein hydrolysis occur principally under conditions of high moisture and elevated temperatures. This type of error can best be prevented by drying the sample at low temperatures until the bulk of the water has been removed and the possibility of the reaction reduced to a minimum. The substance can then be dried at the desired elevated temperature. This is the accepted practice in Europe for determination of moisture in starch.

When incomplete removal of moisture is suspected from substances previously treated with such solvents as alcohol or acetone, it is likely that these solvents, and not water, have resisted volatilization by the thermal drying method. Increase of temperature or change in the pressure of the vapor through vacuum or other means is usually ineffectual. The best remedy is to humidify the sample, in which process the solvent is replaced by water and then this is removed by the accepted thermal method.

To prevent errors from oxidative changes, the simplest method is to use an oxygen-free, inert gas—nitrogen or carbon dioxide—in the thermal drying chamber.

For substances that undergo thermal decomposition there is usually a critical temperature at which this occurs at sufficient rate to introduce errors in the moisture values. In many instances it is possible to determine the critical temperature of decomposition of a substance and, knowing this, to use temperatures in a range below this value for thermal drying.

In thermal drying there are additional sources of error. One of these is slowness in establishing equilibrium between the vapor pressure of the water of the solid and that of the atmosphere. Because we are primarily concerned with absolute dryness, it is not necessary to discuss the effect of exposure of substances to atmospheres of different relative humidities and the time required for equilibration. However, as a substance is being dried and the moisture content approaches zero, the vapor pressure and consequently, the rate of volatilization of the water become very slow. The resulting changes in weight of the substance or weight of water absorbed are so small that the conditions of constancy are assumed to have been fulfilled. Actually, the substance may still contain measurable quantities of water, as in the

case of lactose hydrate or starch. This error can be avoided or by drying for a longer time, using a higher drying temperature, or both.

The formation of a crust which is impervious to moisture has always been a source of error. In the moisture analysis of high sugar samples, sirups, and the like, by thermal drying, a water-impervious crust almost always forms, causing nearly complete stoppage of evaporation of the remaining moisture. This error can be eliminated by use of sand dishes to increase the exposed surface or by top drying at moderate temperatures under infrared heat lamps.

Many plant materials tend to crust before drying is completed, making it difficult or impossible to remove all the moisture. This cause of error can be partially eliminated by drying first at low temperature to remove most of the water without crust formation, and completing the drying at the requisite elevated temperature.

The physical structure of plant or animal tissue may also contribute to errors in drying. Both sorts of tissue often contain as high as 60 to 90% moisture. The removal of moisture from the cells, vacuoles, and tubes of these tissues presents separate problems. Cell moisture must diffuse through the cell wall before it can be volatilized. This becomes increasingly difficult as the drying proceeds. The moisture leaves the surface of the cells by diffusion and if the material is thick it requires considerable time for this to take place. Furthermore, as the cells lose water and the cell fluid becomes more concentrated, there is a lowering of the vapor pressure of the residual water. To drive the last traces of moisture out of the cells at a reasonable rate, the temperature must be increased, and this often makes the cell walls less permeable to water. Heat also tends to seal the tubes in the tissue, making diffusion of deep-seated water vapor very slow. Often the surface of plant parts, such as stems and twigs, is almost impervious to moisture and all the water has to diffuse out longitudinally. These errors due to physical structure can often be avoided by fine grinding to diminish the distance through which the water vapor must diffuse, and by using multiple stage drying, so that most of the moisture can be removed at temperatures at which the cell walls remain permeable to water.

A common source of error in moisture analysis is in sampling, particularly for substances with high moisture content. These samples usually have water vapor pressures much higher than the ambient air, and therefore undergo rapid changes. A typical example is freshly cut leaves. With such material having a water content of 90% or more, an error of sampling which accounts for only a 1% error in moisture can cause a 10% error in the nonvolatile constituents reported on a moisture-free basis. Sampling errors are not specific to thermal methods of moisture analysis, but are inherent in all methods; this is a subject broad enough for consideration in other symposia.

A wide variety of ovens or drying chambers has been designed. To answer the question, "Which ovens are best for moisture analyses?" the following must be considered: Is the moisture present only as surface moisture, is time of drying a factor, and is the moisture deep-seated, as in cells, vacuoles, or capillaries?

If the moisture is loosely held liquid water, almost any type of drying will give satisfactory results. If the water is surface water and time of drying is an important item, elevated drying temperatures are required, but these must be held below the thermal decomposition point of the substance being dried. In drying at atmospheric pressure, time can be gained by using mechanical convection, which removes vaporized moisture from the area of the sample immediately upon vaporization, and reduces to a minimum the time for diffusion of the vaporized water. Drying is usually about four times as fast in mechanical convection ovens as in gravity convection ovens. The former also tend to maintain much greater uniformity of temperature throughout the oven drying chamber. When the moisture is deep-seated

And must diffuse largely through the capillaries, a decided advantage may be gained through the use of vacuum drying.

CONCLUSIONS

Ideal conditions for thermal drying are: using diminished pressure to minimize time of diffusion of deep-seated moisture; using properly desiccated air to sweep the water vapor from the drying chamber; and heating the specimen at a temperature as close as possible to that at which the rate of thermal decomposition becomes appreciable. These conditions provide the maximum difference between the vapor pressure of the water in or on the substance and that of the air in the dryer. It is the magnitude of this difference, together with changes in moisture-vapor diffusion rates, that determines the rate of drying and the degree of drying possible by thermal methods.

LITERATURE CITED

- (1) International Critical Tables, Vol. 3, p. 385, New York, McGraw-Hill Book Co., 1928.
- (2) Katz, J. R., *Kolloidchem. Beihefte*, 9, 1-182 (1917).
- (3) Makower, B., Chastain, S. M., and Nielsen, E., *Ind. Eng. Chem.*, 38, 725 (1946).
- (4) Mellon, E. F., Korn, A. H., and Hoover, S. R., *J. Am. Chem. Soc.*, 69, 827 (1947).
- (5) Nelson, O. A., and Hulett, G. A., *J. Ind. Eng. Chem.*, 12, 40 (1920).
- (6) Pidgeon, L. M., and Maass, O., *J. Am. Chem. Soc.*, 52, 1053 (1930).
- (7) Porter, W. L., and Willits, C. O., *J. Assoc. Offic. Agr. Chemists*, 27, 179 (1944).
- (8) Reith, J. F., Mossel, D. A. A., and Van de Kamer, J. H., *Anal. Chim. Acta*, 2, 359 (1948).
- (9) Sair, L., and Fetzer, W. R., *Cereal Chem.*, 19, 633 (1942).
- (10) Urquhart, A. R., and Eckersall, N., *J. Textile Inst.*, 21, T499 (1930).